

PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Treatment of Leather.

We, RHOM & HAAS COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of 222 West Washington Square, Philadelphia 5, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with impregnated leathers and the improvement of leather by a treatment which involves an impregnation thereof with certain materials for the purpose of preparing it for finishing. It is particularly concerned with a treatment which provides leathers having improved break, fuller substance, and improved resistance to abrasion and scuffing.

It is already known to impregnate leathers with organic solvent solutions of certain polymeric substances and plasticizers therefor. The products obtained by such treatments tend to change with time as plasticizer migration into the leather is gradually lost. When aqueous systems are employed with vegetable-tanned leathers, especially case and upholstery leathers where large amounts of uncombined tannins are present, the penetration is hindered by the swelling and consequent pore-blocking caused by the aqueous systems.

It has been found that leathers can be improved in break and resistance to scuffing by impregnation of the leather with an organic solvent solution of certain copolymers without the use of plasticizers.

In accordance with the present invention, there is provided a process for treating leather which comprises impregnating the leather on the grain side only with an organic solution containing a water-insoluble copolymer of monoethylenically unsaturated molecules comprising (a) 3.5 to 18.5 (preferably 6 to 12.5) mol per cent of at least one acid which is acrylic, methacrylic or itaconic acid, (b) 1.5 to 8 (preferably 1.5 to 5) mol per cent of at least one ester of acrylic or methacrylic acid with a saturated monohydric aliphatic alcohol having 8 to 18 carbon atoms, (c) from 10.5 to 43 (preferably 16 to 27) mol per cent of at least one methacrylate which is methyl, ethyl, or isobutyl methacrylate, and (d) 32 to 84.5 (preferably 58.5 to 80) mol per cent of at least one ester of acrylic acid with a saturated monohydric alcohol having 1 to 4 carbon atoms, the total of (a) and (c) being 15 to 45 mol per cent and the mol ratio of (b) to (c) being from 1:3.3 to 1:6.7, the balance, if any, of said monoethylenically unsaturated molecules being composed of compatible molecules as hereinafter defined, the copolymer having a viscosity average molecular weight of at least 10,000 and a viscosity not exceeding 20 centipoises in a 20% solution at 25° C. in the organic solvent in which it is applied, and the impregnation being effected to penetrate through the corium minor and to deposit copolymer down to the junction of the corium minor with the corium major but to leave the remaining thickness of the leather substantially free of copolymer.

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The copolymers used in the process of the present invention for impregnating leather are formed of at least four different monomers, as is clear from the definition above. Each is essential, as equivalent effects cannot be obtained if one of the four types is omitted. The acid component (a) provides sites in the copolymer having a peculiar affinity for the protein component of the leather fibers, favoring retention of the copolymer in the leather even when it is soaking wet, as from rain. It also reduces the susceptibility of the copolymer to migration when a subsequently-applied coating composition in an organic solvent is applied during finishing. The inclusion of component (b), the higher acrylate or methacrylate esters, imparts flexibility and also solubility in non-polar hydrocarbon solvents and has a distinct advantage, as pointed out hereinafter, in that it reduces swelling of the leather and favors penetration. The hardening component (c), represented primarily by methyl methacrylate, is essential to avoid excessive softness, stickiness, and gumminess of the surface of the impregnated leather. It is also essential to provide the desired "break" improvement. Without this component, little or no improvement in break is obtained. It is also essential that the sum of the acid and hardening components (a) and (c) in the copolymer amount to at least 15 mol per cent in order to obtain the desired break improvement. On the other hand, the sum of these two components must not exceed 45 mol per cent in the copolymer; otherwise, the impregnated leather shows severe grain cracking and boardiness and feels like a plastic sheet instead of leather. The ratio of components (b) and (c) specified above must also be observed if an improvement in break and resistance to scuffing are to be obtained while retaining the desirable leather properties including the temper, well-rounded feel, flexibility, fullness, and susceptibility to be manipulated efficiently in manufacturing operations, including adaptability to be die-cut smoothly and evenly without difficulty. It is to be noted that polymers of components (b) alone, (d) alone, or of a mixture of (b) and (d) or of any of these types even with (a) provide little or no improvement in break and generally provide other undesirable qualities as well, such as excessive softness or looseness, waxy, rubbery, or gummy instead of leathery feel. The monoethylenically unsaturated monomer molecules of which the copolymer is formed may include, in addition to components (a), (b), (c) and (d), other molecules which are referred to above as being compatible. For the purposes of this Specification on this latter term means, of course, molecules which do not vitiate the desirable properties imparted to the copolymer by

components (a)—(d), the desirable properties in question being those discussed above.

Examples of other compatible monomer molecules are those of acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, and vinyltoluene or mixtures thereof. These monomer molecules may be used in an amount up to 32.5 mol per cent. Also, small amounts of neutral hydrophilic comonomers may be included such as hydroxy-ethyl acrylate, acrylamide, methacrylamide, or N-methylolacrylamide. The maximum permissible amount of such hydrophilic comonomers will generally be 5 mol per cent of the total weight of copolymer, but since the upper limit is dictated by the requirement that the copolymer be insoluble in water, in some cases more than 5 mol per cent may be allowable.

It has previously been stated that the average molecular weight of the copolymer should be at least 10,000 but should not be so high nor should the molecular weight distribution be such that the viscosity of a 20% solution at 25° C. in a solvent system by which it is to be applied exceeds 20 centipoises. As to these requirements, the viscosity is measured on a Brookfield Synchroelectric viscometer model LVT using a No. 1 spindle at 60 rpm. and the molecular weight is measured by the method described in Principles of Polymer Chemistry, P. J. Flory, Cornell University Press, 1953, pages 308—315.

The improvement of fullness and feel afforded by the present invention is especially noticeable on the skins of smaller animals, such as sheep, goats and pigs, making them suitable for such products as certain types of shoe leathers for which only the skins of larger animals as cowhides, steerhides, and horsehides have heretofore generally been considered suitable. The process of the present invention also has the advantage that it in many cases reduces the need for retannage or completely eliminates such need.

The solvents that may be used include alcohols, ketones, ethers, esters, ether-alcohols, hydrocarbons and chlorinated hydrocarbons. Examples of alcohols include ethyl alcohol, methyl alcohol, isopropyl alcohol, and *tert*-butyl alcohol. Examples of ketones include acetone, methyl ethyl ketone, methyl isopropyl ketone, diisobutyl ketone, methyl isobutyl ketone and ethyl isopropyl ketone. Examples of ethers include dioxane, diethyl ether, tetrahydrofuran and diisopropyl ether. Examples of esters include ethyl acetate, isopropyl acetate, butyl acetate, 2-ethoxyethyl acetate, 2-butoxyethyl acetate, ethyl propionate, and methyl butyrate. Examples of ether-alcohols include diethylene glycol, the mono-ethyl ether of diethylene glycol, and also the monomethyl, monopropyl, and

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monobutyl ethers of diethylene glycol. Examples of hydrocarbons include benzene, toluene, xylenes, petroleum and solvent naphthas of aromatic character and mixtures of these aromatic with aliphatics such as octane and decane. Chlorinated hydrocarbons include methylene chloride, ethylene dichloride, perchloroethylene, chloroform, bromoform, and carbon tetrachloride.

The particular solvent may be composed of a single solvent material or it may be composed of a mixture of any of the materials mentioned hereinabove. Preferred solvents are the hydrophobic types of hydrocarbon or halogenated hydrocarbon type. These solvents have the advantage of not swelling the leather or its components and thereby avoiding the tendency of the solvent-soaked components to swell and block the pores and hinder the penetration of the solution of the polymer. All of the organic solvent systems, whether of hydrophobic character or of the other types mentioned hereinabove, are characterized by substantially less tendency to swell the components of the leather than is generally associated with aqueous media.

The copolymers may be prepared in any suitable fashion provided they are of proper molecular weight as defined hereinabove. Such copolymers are readily produced by copolymerization in suitable solvents, including any of those mentioned hereinabove. The solvent that is to be employed for the impregnation of the leather may be used in the preparation of the copolymer itself so that there is no need to recover the polymer from the initial solution formed and to redissolve such polymer.

The choice of proportions of the comonomers to be used depends in part upon the flexibility or firmness desired in the product. By using a large total proportion of components (b) and (d), highly flexible products are obtained without the use of plasticizers, whereas a low total of (b) and (d) within the ranges indicated imparts greater firmness without causing undesirable stiffening or grain cracking. The use of the several components of the copolymer in the preferred range specified herein provides the optimum combination of properties obtainable by the present invention.

The concentration of the copolymer solution may vary widely. For example, concentrations of 10 to 30% may be employed for most of the copolymers. The use of higher concentrations up to 35% may be permissible with the copolymers of extremely low molecular weight, whereas it may be necessary to use concentrations even lower than the lower limit of the range mentioned when the copolymer is of molecular weight near the upper limit of the range given above. In

general, the solution contains at least 10% by weight of copolymer.

The copolymer solution may also contain additional materials such as dyes, pigments, and other polymeric materials in small proportions. The amount of such additional polymeric substances should be kept relatively low as compared to the copolymer, and it is preferably not over 25% of the weight of the copolymer. The use of a dye or a pigment is sometimes desirable to reduce the number of subsequent finish coatings when a colored leather is to be produced. The proportion of pigment, however, should not be enough to hinder the entry and penetration of the copolymer solution into the leather and thus prevent the complete penetration of the copolymer through the thickness of the corium minor. In general, the amount of pigment should not exceed 15 parts per 100 parts by weight of the solution used for impregnation.

Non-plasticizing oils may also be included in the impregnating solution. The solvent solution application offers advantages over aqueous impregnation in that the leather fibers are not swollen during application of the impregnating polymer and thus do not form adhesions during the drying process. However, if the leather is to be subsequently wet with water, e.g., by the application of aqueous finishing coats, it is sometimes useful to apply oils which lubricate the leather. These replace the leather fat liquor which was originally present in the grain surface of the leather and which reduces such "aqueous" adhesions but which can be driven from the grain surface by the application of the solvents in the impregnating mixture.

Natural oils such as neatsfoot, coconut, sperm and cod oils can be employed as leather lubricants. Such oils tend to migrate on later flexing of the leather but can be prevented from doing so by the addition of a long-chained solvent-soluble molecule containing a polar group. Examples of the latter are oleic acid, alkenyl succinic acid anhydrides such as octadecenyl, primary tallow amine, (C₁₈-C₂₂)-alkylamines, such as tertiary-dodecyl amine, tertiary-pentadecyl amine, and mixtures thereof, and the monoglyceridyl glycolates of natural oils such as neatsfoot monoglyceridyl glycolate. In general, $\frac{1}{10}$ th as much polar constituent as of non-polar natural oil is required to prevent migration of the oil mixture during flexing of the leather. The total concentration of oils in the impregnation mixture is usually 3-7%.

The copolymer solution may be applied in any fashion provided it is applied under such conditions that time is available for adequate penetration before extensive drying of the solution occurs. In the preferred

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method, the solution is swabbed, brushed, or sprayed on the grain surface only of the leather. The swabbing, brushing, or wiping action employed may be extended in duration as the means to assure adequate penetration and deposition, and, for this purpose, the normal equipment that is used simply for coating leather is ordinarily inadequate, since such equipment involves a mere brushing to spread the coating evenly over the surface followed substantially immediately by drying. For the purpose of accomplishing the impregnation by a brushing operation, it is necessary that the brushing be continued for a comparatively extended period of time while the impregnating material is applied to the surface of the leather and maintained thereon in wet condition. Thus, an extended period of concurrent application and brushing should be carried out to prevent the drying of the material on the surface before extensive penetration can be accomplished. Hence, ordinary spraying or seasoning equipment for leather coatings cannot be employed without modification. Specially designed equipment capable of applying heavy amounts of organic solvent solutions of polymer may be utilized.

The copolymer solution may be applied by drumming.

More or less of the copolymer may be left as a coating upon the leather at the end of the impregnation process, depending upon the particular manner of effecting the impregnation. However, whether or not a substantial amount of polymer material is left at the surface, it is essential that the copolymer be forced to penetrate through the corium minor or grain layer and to deposit the copolymer within the entire thickness thereof and at the junction with the corium major. Mere filling of hair pockets with the copolymer will not suffice. Although it is not essential to follow the impregnation treatment of the present invention with a finishing treatment involving the application of one or more coats of a finishing composition, it is generally preferred to provide such a finishing treatment.

The impregnation may be effected at room temperature or at somewhat elevated temperatures up to 80° C., the higher temperatures being particularly useful when it is desirable to obtain an even lower viscosity with a given concentration of certain of the copolymers.

After deposition of the copolymer within the body of the leather, the leather may be simply allowed to dry by evaporation of the organic solvent at room temperature or removal of solvent may be accelerated by heating to somewhat elevated temperatures such as 50 to 70° C. On removal of the organic solvent the dry water-insoluble acid

copolymer is left within the body of the leather.

The invention is, of course, applicable to full-grain leathers, but more particularly it is suited to snuffed or buffed grain leathers and improves the break characteristic of leathers of these types, as well as improving the resistance to scuffing and abrasion. It also renders the subsequently finished leathers more readily repaired if any scuffing penetrates through the finish coats.

The ability of the solution to penetrate the leather depends upon the viscosity and surface tension of the ingredients and their proportions. Viscosity can be lowered by proper selection of the solvent and by increasing the amount of solvent. However, the desirable viscosity in a particular application depends also upon the porosity of the leather in a particular application. This, in turn, is affected by many factors, such as the type of skin, i.e., calf, cowhide, or goat, the method of tanning, the extent of the tannage, the condition of tanning, such as pH, the oil and grease content, previous processes such as liming and bating, the mechanical handling of the skin and the tanning and drying processes, such as setting out and staking, and the amount of buffing.

The depth of penetration is controlled primarily by the amount of solution applied, once the penetrability of the solution has been regulated so as to allow it to penetrate in the first place. The depth of penetration is increased with increasing amounts of solution. Cowhide upper leather will absorb roughly its own weight of liquid. Since a penetration of at least 15% of the thickness of the leather is generally required for best results, depending on the proportion of corium minor to corium major, a 15% penetration of cowhide corresponds approximately to application of liquid solution in weight of 15% of the weight of the leather, and correspondingly for other proportions. Furthermore, a small amount of penetration of less than three to five per cent of the thickness of the leather can be worse than no treatment and can result in a very coarse break, which is undesirable.

As between individual skins of a particular type to be treated, particularly sheepskin, the total thickness of the skin will vary and, therefore, the proportion of thickness of the grain layer to total thickness of the skin may vary considerably. Therefore, an average quantity of solution per unit of area must be determined and used for a particular run. For instance, in a particular run the variation of grain layer thickness to total skin thickness may vary from 20% to 40% and the optimum penetration for the run will then be determined at 30%.

As previously stated, a small degree of penetration with respect to thickness is more

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likely to be harmful than beneficial. It is recognized that attempts have been made to improve the characteristics of leathers by impregnation of the entire thickness of the leather. However, such total thickness impregnation must also be avoided in the present process because, in addition to the substantially greater cost of material involved, in total thickness impregnation the natural characteristics of the leather are impaired. For instance, it is desirable that shoe upper leather be capable of absorbing perspiration vapor and dispersing it to the outside. For this purpose, high quality shoe upper leather has absorptive qualities and vapor permeability and these characteristics are inhibited little, if any, by our process of partial impregnation, whereas total thickness impregnation markedly reduces the moisture absorptive property and vapor-permeability of the leather.

The non-impregnated thickness of the leather product of the present invention is substantially free from the copolymer so that its vapor-permeability and flexibility are not substantially affected by the treatment. It is believed that this is one of the reasons why the overall vapor-permeability and flexibility of the treated product throughout its entire thickness are not reduced to such an extent as to make the product unsuitable for use as shoe uppers, as is the case when the entire leather thickness is impregnated with the resin solution of the present invention. However, it will be appreciated that comparatively small quantities of copolymer may be present in the remaining thickness, or on the flesh surface, of the leather without reducing the natural flexibility and vapor-permeability thereof sufficiently to make the overall flexibility and vapor-permeability unsatisfactory. For example, the leather may have small holes or cuts passing from the grain surface into the flesh layer through which the solution flows when it is applied to the grain surface. Consequently, when it is stated herein that the remaining thickness of the leather is "substantially free from copolymer," it is meant that such remaining thickness does not contain a sufficient amount of copolymer to modify materially the natural properties thereof and it is not intended by such term to exclude small quantities of copolymer in such remaining thickness which are insufficient to reduce the vapor-permeability and flexibility properties thereof to a degree which will render the overall flexibility and permeability of the leather product unsuitable for the purposes set forth. Furthermore, the statement used herein that the copolymer solution is applied "to the grain surface only" does not exclude any kind of treatment which results in such small quantities of copolymer being present in the remaining thickness of the finished product.

The impregnation of the present invention is adapted to be applied to any type of leather such as that obtained from the skins of calves, cattle, goats, sheep and horses, and regardless of the particular manner of tanning. Thus, the leather may be that obtained by chrome tanning, zirconium tanning, vegetable tanning, or tanning by the use of synthetic tanning agents. It is particularly valuable with chromium-tanned leather. At the time of the application of the impregnation, the leather should generally be that obtained after the drying of the tanned, dyed, and/or fat-liquored leather.

The impregnation treatment of the present invention improves the break, the filling, and the resistance to abrasion and scuffing of the leather. The improvement is such that, even with tanned leathers of poor quality, impregnated leathers of high quality can be obtained that are suitable for use as shoe uppers, shoe linings, handbags, belts, garments, gloves, luggage, footballs, baseballs, bookbindings, upholstery and other related uses. The improvement in the break referred to is so outstanding that inferior grades of leathers which command a low price because they ordinarily cannot be finished into high quality leather having good break characteristics can be treated by the present invention and converted into high quality leathers having good characteristics as far as break is concerned. In other words, the present invention serves to upgrade leathers, whether the inferiority of the leather treated is that inherent in the particular hide from which the leather was produced or that resulting from the tanning and/or other operations by which it was produced. Because of this capacity of the present invention, it may be applied to the leathers obtained from loose flanks and bellies which are ordinarily of such inferior grade that they have been discarded or used only as so-called "offal" leathers. When applied to such poor grade materials, the finished leathers that can be obtained are so improved in quality that they can be used for the making of shoes, upholstery, bags, belts and briefcases, where high-grade leathers are needed. In addition, sufficient filling action is provided by the copolymer to firm the loose areas such as bellies and flanks of the leather so that more of these articles of commerce can be obtained from the leather than would otherwise be possible.

After application of the impregnation, whether or not it involves the leaving of any of the copolymer on the surface, the leather may be, and preferably is, finished by the application of one or more coatings. This subsequent coating may be any polymeric or other material normally employed for

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leather finish coatings. It may, of course, be pigmented, dyed, or not, as desired. Conventionally used finishing materials such as nitrocellulose lacquers or aqueous disper-

sions or organic solvent solution of vinyl or acrylic polymers have been found suitable for finishing such impregnated leathers.

In finishing, the surprising discovery was made that the adherence of these leather finishes to such impregnated leather was better than to the surface of the same leather prior to impregnation. In addition, the wet-molding qualities of the finished impregnated leathers are greatly enhanced. This is particularly the case when the leather is plated after application of one or more finish coats.

The process of the present invention includes the application of hydrophilic acid copolymers to leather in an organic solvent system that is adapted to provide a flexible leather which is not characterized by undesired stiffness.

The process of the present invention is

50	Ethyl acrylate, inhibited with 200 ppm of monomethyl ether of hydroquinone	20.47 lbs. (0.205 lb. mole)
	Methyl methacrylate, inhibited with 60 ppm of monomethyl ether of hydroquinone	6.3 lbs. (0.063 lb. mole)
55	Methacrylate derived from a mixed technical alcohol mixture which was 2% tetradecanol, 30% hexadecanol, and 68% octadecanol, uninhibited, 98% pure by saponification number	3.22 lbs. (0.010 lb. mole)
	Methacrylic acid, inhibited with 250 ppm of monomethyl ether of hydroquinone	1.57 lbs. (0.018 lb. mole)

A catalyst solution was also made up in another vessel consisting of:

Toluene	6.93 lbs.
Benzoyl peroxide	0.788 lbs.

Concomitant addition of 20% of the monomeric mixture and 20% of the catalyst solution was then made to the polymerization kettle and a batch temperature of 108—103° C. was maintained for 20 minutes before the rest of the monomeric solution and catalyst solution were added gradually and concomitantly during 100 minutes. The batch temperature was maintained at 110°—111° C. for 4½ hours; thereafter at 100°—

adapted to produce leathers having improved break and scuff resistance without the necessity of employing an alkaline aqueous medium for the impregnation of the leather which tends to swell some types excessively, thereby tending to provide non-uniform impregnations and to slow down the rapidity of impregnation.

In the following examples which are illustrative of the invention, the parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

(a) *Preparation of Copolymer.* A stainless steel kettle was fitted with an agitator, a thermocouple, an inlet pipe for nitrogen gas, a pot for holding the monomer, a funnel for a catalyst solution, a water-cooled condenser, and a steam-heated jacket.

The polymerization vessel was flushed with nitrogen and charged with 34 lbs. of toluene and 3.83 lbs. of cumene, which mixture was heated to 105—110° C. A monomeric mixture was made up consisting of:

101° C. for 2½ hours. At 7 hours, 5.07 lbs. of toluene was added and the batch allowed to cool to 30° C. The product was a toluene:cumene solution containing 40.2% of copolymer. The yield of solids in the solution was 74 lbs., 2 ozs. At 25° C., the viscosity of the 40.2% solution, as measured on a "Synchro-Lectric" Brookfield viscometer, was 63 centipoises. The flash point (Tag) was 54° F. The viscosity at 25° C. in the same solvent but at 20% concentration was 7.4 cps.

(b) Higher flash points are obtained when the copolymer is made in other solvents. For example, the following runs gave the following results:

Run	Solvent	% Solids	Visc. 20% cps	Flash point Found
A	Solvesso 150 (a high flash high aromatic solvent naphtha boiling in the range of 369 to 406° F.)	40	7.9	125° F. Tag.
B	Solvesso 150/toluene = 95.6/4.4 (weight ratio)	40	7.5	160° F. Tag.
C	Solvesso 100 (a high flash high aromatic solvent naphtha boiling in the range of 321 to 349° F.)	40	6.7	118° F. Open Cup

The word "Solvesso" is a Registered Trade Mark.

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(c) An impregnation mixture was applied to bad-breaking, full-grain, chrome-tanned, lightly vegetable-retanned calfskin by swabbing on two wet coats with a felt swab. The first coat was applied with a dripping wet swab which was rewet often to keep it saturated. Then, before the polymer could "set" or dry due to the absorption of the solvent by the leather, a second wet coat was applied in a similar fashion. Uptake of the solvent solution by the leather was 38% of its original dry weight. The composition of the impregnation was as follows:

Ingredients	Parts by weight
Polymer Solution (of part a) ...	73.2
Toluene ...	26.8
Neatsfoot oil (20° cold test) ...	10.0
Oleic acid ...	1.0
Total	111.0

The leather was dried and then finished with a conventional plated black finish. It was compared with other calfskins from the same lot of leather which had been similarly finished. The unimpregnated calfskins all showed good break near the backbone which rapidly worsened as tests of leather break were made at intervals moving out toward the periphery of the hide. Even the median area between backbone and flanks showed poor break on these skins. The flank area itself was loose and very bad breaking. The overall appearance and feel of the unimpregnated leathers was flat and a little un-leatherlike and papery in feel.

The impregnated finished leather on the other hand showed a fine, tight, rolling break in all parts, even in the flank areas. The leather felt full and supple throughout. This fullness was outstanding in the flank areas in contrast to the unimpregnated skins.

Scuff resistance of the impregnated leather was outstanding. Vigorous scuffing across the unimpregnated leathers with a United States coin of 50 cents denomination produced extensive rupture of fibers. However, a similar scrubbing across the impregnated leather produced no change except for a slight increase in gloss where it had been scrubbed. Prolonged scrubbing led to melting of the finish from the frictional heat before fiber rupture occurred.

EXAMPLE 2

(a) A copolymer was made by a process similar to that in Example 1(a), except that the monomer composition was:

Ethyl acrylate ...	61 mol %
Methyl methacrylate ...	28 mol %

Methacrylate from same mixed alcohol mixture as in Example 1 ...	5 mol %
Methacrylic acid ...	6 mol %

The copolymer was prepared in Solvesso 100. The final concentration was 40% and its viscosity at that concentration was 99 cps. After dilution to 20% with Solvesso 100, its viscosity was 9 cps.

(b) An impregnation mixture was applied to bad-breaking, buffed, chrome-tanned, vegetable-retained steer hide by swabbing on two wet coats with a felt swab in a manner described in Example 1 (c). Uptake of the solvent solution by the leather was 36% of its original weight.

The composition of the impregnation mixture was as follows.

Ingredients	Parts by weight
Polymer solution from section (a) of this example ...	100.0
Solvesso 100 ...	48.0
Raw Neatsfoot oil (20° cold test) ...	6.0
Oleic acid ...	0.6
Total	154.6

The leather was dried and then finished with a conventional black shoe upper leather finish and was compared with an unimpregnated but similarly finished adjacent section of leather from the same hide. The impregnated leather showed improved break characteristics and improved scuff resistance over the unimpregnated section without noticeably detracting from the leather temper.

EXAMPLE 3

Polymers were prepared in appropriate solvents by the procedure of Example 1 (a) from mixtures of monomers in the proportions given hereinbelow:

(a)	3.5 mol % of itaconic acid	
	30 mol % of ethyl methacrylate	
	4.5 mol % of octadecyl acrylate	
	62 mol % of butyl acrylate	105
(b)	12 mol % of acrylic acid	
	33 mol % of isobutyl methacrylate	
	8 mol % of n-octyl acrylate	
	47 mol % of methyl acrylate	110
(c)	3.5 mol % of itaconic acid	
	12.5 mol % of methyl methacrylate	
	5 mol % of vinyltoluene	
	5 mol % of dodecyl acrylate	
	74 mol % of ethyl acrylate	115

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- (d)*
 3.5 mol % of itaconic acid
 12.5 mol % of methyl methacrylate
 10 mol % of vinylidene chloride
 5 mol % of dodecyl acrylate
 69 mol % of ethyl acrylate
- (e)
 3.5 mol % of itaconic acid
 12.5 mol % of methyl methacrylate
 6 mol % of acrylonitrile
 5 mol % of dodecyl acrylate
 73 mol % of ethyl acrylate
- (f)
 3.5 mol % of itaconic acid
 12.5 mol % of methyl methacrylate
 2 mol % of vinyl acetate
 2 mol % of vinyl chloride
 2.5 mol % of acrylonitrile
 50 mol % of ethyl acrylate
 22.5 mol % of methyl acrylate
 5 mol % of dodecyl acrylate

* In part (d), the benzoyl peroxide was replaced with azodiisobutyronitrile as the catalyst.

- 25 Impregnating compositions were made from each of the polymers prepared from the mixtures (a) to (f) of Example 3 by diluting the copolymers with a mixture of xylene and ethylene dichloride to form 22% solutions. The solutions were applied in the same manner as described in Example 1 (c). The leathers thus impregnated were tested in the same manner as in Example 1 (c). Similar improvements in break and scuff resistance were obtained while retaining desirable leather temper.

WHAT WE CLAIM IS:—

1. A process for treating leather which comprises impregnating the leather on the grain side only with an organic solvent solution containing a water-insoluble copolymer of monoethylenically unsaturated molecules comprising (a) 3.5 to 18.5 mol per cent of at least one acid which is acrylic, methacrylic or itaconic acid, (b) 1.5 to 8 mol per cent of at least one ester of acrylic or methacrylic acid with a saturated monohydric aliphatic alcohol having 8 to 18 carbon atoms, (c) from 10.5 to 43 mol per cent of at least one methacrylate which is methyl, ethyl, or isobutyl methacrylate, and (d) 32 to 84.5 mol per cent of at least one ester of acrylic acid with a saturated monohydric

alcohol having 1 to 4 carbon atoms, the total of (a) and (c) being 15 to 45 mol per cent and the mol ratio of (b) to (c) being from 1:3.3 to 1:6.7, the balance, if any, of said monoethylenically unsaturated molecules being composed of compatible molecules as hereinbefore defined, the copolymer having a viscosity average molecular weight of at least 10,000 and a viscosity not exceeding 20 centipoises in a 20% solution at 25° C. in the organic solvent in which it is applied, and the impregnation being effected to penetrate through the corium minor and to deposit copolymer down to the junction of the corium minor with the corium major but to leave the remaining thickness of the leather substantially free of copolymer.

2. A process as defined in Claim 1 in which the copolymer also comprises up to 32.5 mole per cent of molecules of at least one of the following monomers, namely: acrylonitrile, methacrylonitrile, vinyl acetate, vinyl chloride, vinylidene chloride, styrene, and vinyl toluene, as compatible molecules.

3. A process as defined in Claim 1 or 2 in which the copolymer also comprises up to 5 mol per cent of at least one neutral hydrophilic monomer which is hydroxyethyl acrylate, acrylamide, methacrylamide, or N-methylolacrylamide.

4. A process as defined in any one of Claims 1—3, wherein the copolymer is a copolymer of molecules comprising 6 to 12.5 mol per cent of component (a), 1.5 to 5 mol per cent of component (b), 16 to 27 mol per cent of component (c), and 58.5 to 80 per cent of component (d).

5. A process as defined in any one of Claims 1—4, wherein the solution contains at least 10% by weight of said copolymer.

6. A process according to Claim 1 substantially as hereinbefore described with reference to any one of the foregoing Examples.

7. A leather treated by a process according to any one of Claims 1—6.

8. A leather having, distributed through the corium minor, a water-insoluble copolymer as defined in any one of Claims 1—4; the remaining thickness of the leather being substantially free of said copolymer.

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